DOE/PC/89869--T13

89869-T13

DEVELOPMENT OF A STABLE COBALT-RUTHENIUM FISCHER-TROPSCH CATALYST

CONTRACT DE-AC22-89PC89869

Technical Progress Report No. 14
01/01/93-03/31/93

prepared for

Pittsburgh Energy Technology Center
Department of Energy
Pittsburgh, Pennsylvania

prepared by

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Des Plaines, Illinois

DEVELOPMENT OF A STABLE COBALT-RUTHENIUM FISCHER-TROPSCH CATALYST

Contract DE-AC22-89PC8969

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Contract Objective

The objective of this contract is to examine the relationship between catalytic properties and the function of cobalt Fischer-Tropsch catalysts and to apply this fundamental knowledge to the development of a stable cobalt-based catalyst with a low methane-plus-ethane selectivity for use in slurry reactors.

Contract Tasks

Task 1.0: Project Management Report
Task 2.0: Reference Cobalt (Co) Catalyst
Task 3.1: Modifier Role for Ruthenium (Ru)
Task 3.2: Particle Size Effects with Ru
Task 4.1: Identification of Synergy between Co and a Second Bimetallic Element, such as Ru
Task 4.2: Development of a Bimetallic Catalyst
Task 5.0: Demonstration of Stability

Experimental

The fixed bed pilot plant, the catalyst testing procedure, and the calculations for conversion and selectivities were previously described in the technical progress report covering the period of 3/16/88 to 6/16/88 for Contract DE-AC22-87PC79812. Conversions and hydrocarbon

selectivities were calculated using data from an on line gas chromatograph (GC) which analyzed the gas product. Alcohol selectivities were calculated using data from an on line GC boiling point analyzer which analyzed the liquid product.

The feed for all cobalt catalyst evaluations was a blend of hydrogen, carbon monoxide and argon. The argon was an internal standard required for the conversion and selectivity determinations above. The molar ratio of hydrogen to carbon monoxide was two, which is typical of a methane-derived synthesis gas. A typical feed was comprised of the following mole percentages of gases: hydrogen 64, carbon monoxide 31, argon 5. Because of the sensitivity of Fischer-Tropsch catalysts to feed impurities, pure feeds were purchased from Scott Specialty Gases of Troy, Michigan. Furthermore, prior to use the feed was processed through 1265 cc of alumina spheres at 210° C and 515 cc of 13X zeolites at room temperature.

Catalysts were prepared via the steps of: impregnation, calcination and reduction, this method is outlined in Figure A-1. The support was a special Y-zeolite-derived material. The impregnation step consisted of pore filling with an ethylene glycol solution of metal salts followed by evaporation of the solvent. The calcination step was always four hours at 450° C. The reduction step was the final step before introduction of the Fischer-Tropsch feed. This step was accomplished in the Fischer-Tropsch reactor after the catalyst and a diluent (usually quartz sand) were loaded; it consisted of four hours of flowing hydrogen at 350° C. The diluent aids removal of heat from the very exothermic Fischer-Tropsch reaction.

For all the runs discussed in this report, 13 g of powdery catalyst were loaded with 160 g of 60 to 80 mesh quartz sand. A thermowell was present down the center of the catalyst/diluent bed. A sliding thermocouple in this well allowed bed temperature profiles to be obtained. Previous experimental catalysts were screened via a three condition test. The final two (more strenuous) conditions were needed to achieve high conversions since the catalysts were of low activity. Selectivities must be assessed at high conversions since for cobalt catalysts methane selectivity is often lower at higher conversion. The two catalysts in this report were so active that high conversion data was available at Condition 1. Very little work was done at more strenuous conditions. A goal of the current work is high activity catalysts which exhibit low methane selectivity.

All figures including run summary plots of conversions and selectivities vs. hours-on-stream are attached in Appendix A. Catalyst compositions are shown in Table 1.

Scope of Work During Reporting Period

Two new catalysts were prepared and screened. They were of high initial activity, similar to the reference catalyst resulting from previous contracts to Union Carbide. Evaluation of this catalyst was outlined in Quarterly Report No. 12. The reference catalyst was prepared on a special support which resulted from laboratory steaming followed by laboratory acid-washing of Y-zeolite. The two new catalysts were prepared on a commercial product which is a steamed Y-zeolite that is washed, but not extensively, with nitric acid during its manufacture. Prior to use, this support was further washed with nitric or hydrochloric acid in the laboratory. Metals were impregnated via a pore filling method from ethylene glycol solvent.

The first catalyst was prepared on a support which was washed seventy-two hours with 3M nitric acid. The second one was prepared on a support resulting from a three hour wash with 4M hydrochloric acid. The purpose of acid-washing is to remove pore-obstructing alumina debris which results from steaming. Acid washing must be properly managed; if it is too strenuous the crystallinity remaining after steaming is destroyed and an amorphous silica results. Hydrochloric acid is particularly prone to destroying zeolite crystallinity. A successful acid wash is one which provides a product with nearly the same surface area and pore volume (high crystallinity) as the steamed material before acid washing, but less aluminum, for instance, see Table 1.

One of the two new catalysts contained ruthenium, since it was the objective of this work to determine whether incorporation of a small amount of ruthenium can result in a high activity catalyst.

The specially-prepared Y-zeolite is characterized by pores that are from 50 to 100 Å in diameter. Such pores are large enough to support 50-100 Å cobalt crystallites, a size considered optimal for Fischer-Tropsch catalysis. The reverse micelle impregnation method developed by UOP under a previous DOE contract controls particle size by a different mechanism. It might not be needed for steamed Y zeolite supports, for instance, a reverse micelle impregnated catalyst supported on a steamed and acid-washed Y-zeolite was evaluated in Quarterly Report No. 12. This catalyst was inferior to one prepared via simple aqueous impregnation on the same support.

In previous quarterly reports on this contract catalysts were reported which were prepared on the commercial steamed and lightly acid-washed Y-zeolite with no laboratory washes. These catalysts were less active and more selective to methane than the reference catalyst. In addition, other catalysts were reported which were prepared on steamed Y-zeolite which had been laboratory acid-washed (Quarterly Report No. 12). It was found during evaluation of these latter

catalysts that more extensive acid washes produced material which provided more active catalysts. The Run 87 catalyst from Quarterly Report No. 12 is an example of an active catalyst utilizing an extensively nitric acid-washed, steamed Y-zeolite support. It contained 9.4% cobalt (Table 1), approximately the same level as on previous catalysts including a reference catalyst resulting from previous DOE contract to Union Carbide.

Results and Discussion

Run 95

This run's catalyst was the first during this contract to be prepared by ethylene glycol impregnation. However, many catalysts in the previous Union Carbide contracts used this solvent. It was supported on material from the second batch of 72 hour nitric acid-washed material. There were some small differences in properties between the two batches (Table 1).

In addition to cobalt, this catalyst contained manganese and zirconium (Table 1). These two minor metal adducts enhanced catalyst conversion stability and aided in the reduction of methane selectivity in catalysts developed during the previous Union Carbide contracts. Conversions and selectivities vs. hours-on-stream for this run are in Appendix I as Figures A-2 to A-7. The initial conversions were very high, for instance, the initial carbon monoxide conversion was 100%! In the early part of the run catalyst activity was lost at a fast rate, however, by about 40 hours on stream the rate of loss of activity had slowed appreciably. By 80 hours on stream the catalyst appeared to be nearing a line out at about 63% carbon monoxide conversion. The selectivities also appeared to be approaching line out at this time, for instance, the methane selectivity was about 12 mole %.

The space velocity was halved just before 120 hours-on-stream. This resulted in an increase in the conversions (carbon monoxide conversion = 85%) but also an indication that catalyst activity loss was continuing albeit at a lower rate. The selectivity to light ends decreased as expected since cobalt catalysts are known to produce less methane, ethane, etc. (methane selectivity = 11 mole %) as the conversion increases due to feed rate changes (but not when conversion is changed by changing temperature).

The temperature was increased near the end of the run resulting in a further increase in conversion (carbon monoxide conversion = 98%) but there was indication again that the catalyst was still slowly losing activity. The light ends selectivities increased near the end of the run, probably due to the higher operating temperature (methane selectivity = 12%).

Run 97

This run's catalyst was prepared on a hydrochloric acid-washed support. The hydrochloric acid caused near complete removal of aluminum but little apparent loss in crystallinity from that of the steamed Y-zeolite as judged by the small loss in surface area (Table 1).

Bench experiments had indicated that the highly-washed supports appeared capable of adsorbing greater amounts of metal than earlier catalysts prepared under the current DOE contract or the previous contracts to Union Carbide. Thus the Run 97 catalyst contained about twice as much cobalt as earlier catalysts. In addition, it contained 1 wt % ruthenium.

This catalyst was very active and the initial operating conditions were never changed to enhance the conversion. Conversions and selectivities vs. hours on stream are in Figures A-8 to A-14. As in Run 95 the high initial activity (carbon monoxide conversion = 93%) was lost during what appeared to be a 100 hour line out. The carbon monoxide conversion near the apparent line out was 73% which is 10% higher than the Run 95 catalyst at a similar time during its line out. However, with the exception of the slightly lower butene selectivity, the light ends selectivities were about the same as in Run 95.

The high activity of the catalyst caused a significant exotherm in the catalyst bed in spite of the large amount of quartz sand diluent used in these runs to aid heat removal. Temperature profiles of the catalyst bed at four times during this run are in Figure A-15. The initial exotherm was sufficient to record a catalyst bed maximum temperature 20° C above the inlet temperature. In most of the cases with lower activity catalysts the catalyst bed maximum temperature was only a few degrees above the inlet temperature. This means that the high conversion in Run 97 was due in part to the actual catalyst operating temperatures being above the inlet of 211° C which was, on the other hand, close to the actual operating temperature during the earlier runs with lower activity catalysts.

The changes in temperature profiles as the run progressed are not indicative of catalyst activity loss due to feed impurities. In such cases the feed impurity is usually adsorbed onto the catalyst causing loss of activity by continual destruction of catalyst beginning close to the inlet and proceeding down the catalyst bed as time increases. The gradual loss in temperature at the hot spot without a downward movement of the position of the hot spot is more indicative of loss in catalyst activity due to adsorption of reaction products such as coke or high molecular weight wax, or to gradual destruction of the catalyst active sites due, perhaps, to a thermal effect such as sintering.

Finally, part of the loss in conversion as the run progressed was due to the catalyst operating at a lower temperature as the run progressed due to the changes in the temperature profiles noted above. If heat had been added to maintain the hot spot at 230° C conversion would probably have been lost at a lower rate.

Summary and Implications for Further Work

Catalysts supported on largely crystalline, but steamed and acid-washed Y-zeolite have been prepared and shown to be more active than any prepared previously during this work. These catalysts lost activity at a fast rate during approximately the first 100 hours of processing at the least strenuous condition of the three condition screening test previously used in this work for catalyst screening. However, a line out in activity was eventually approached. At this time the catalysts were still more active than previous ones. The methane selectivity was slightly higher than that of the reference catalyst.

The most active of the two catalysts described herein contained more cobalt than all others in this work to date. Furthermore, it contained a small amount of ruthenium. Either or both of these properties could have been responsible for the superior activity. This catalyst will be employed as a catalyst in the slurry-autoclave pilot plant. In this plant the catalyst operating temperature can be maintained more easily at target since the autoclave typically contains a larger amount of diluent than the fixed-bed plant (290 g of oil) and is continuously stirred so heat cannot build up at one spot. Such evaluation in a slurry phase pilot plant (liquid phase Fischer-Tropsch, LPFT) is also of interest since the ultimate objective of this contract is development of a LPFT catalyst.

TABLE 1
CATALYST PRECURSORS:
SUPPORTED OXIDES ON STEAMED/ACID-WASHED Y ZEOLITES

SUPPORT PROPERTIES			CATALYST NO./ RUN NO.	CATALYST METALS, AAS WT%			
TRTMNTS	SA[1]/PV[2]	Al[3]		Co	Mn	Zr	Ru
STMD	591/0.51 591/0.51 591/0.51	5.24 5.24 5.24	6531-176/80 6531-167/81 6531-166/82	7.5 8.1 7.3	0.4 0.6	1.0 1.0	
STMD/ HNO_3[4]	596/0.54 596/0.54 574/0.51	2.94 2.94 4.01	6531-188/86 6531-186/87 6827-79/95[5]	9.1 8.9 9.4	1.9	0.47	
STMD/ HCl[6]	582/0.56	0.46	6827-81/97	17.6	2.0	1.64	1.01

1. m^2/g
2. cc/g
3. wt %
4. WASH 72 HOURS WITH 3M HNO_3.
5. THIS CATALYST ALSO CONTAINED 0.43 wt% RHENIUM.
6. WASH 3 HOURS WITH 4M HCl.

FIGURE A-1

STANDARD CATALYST PREPARATION

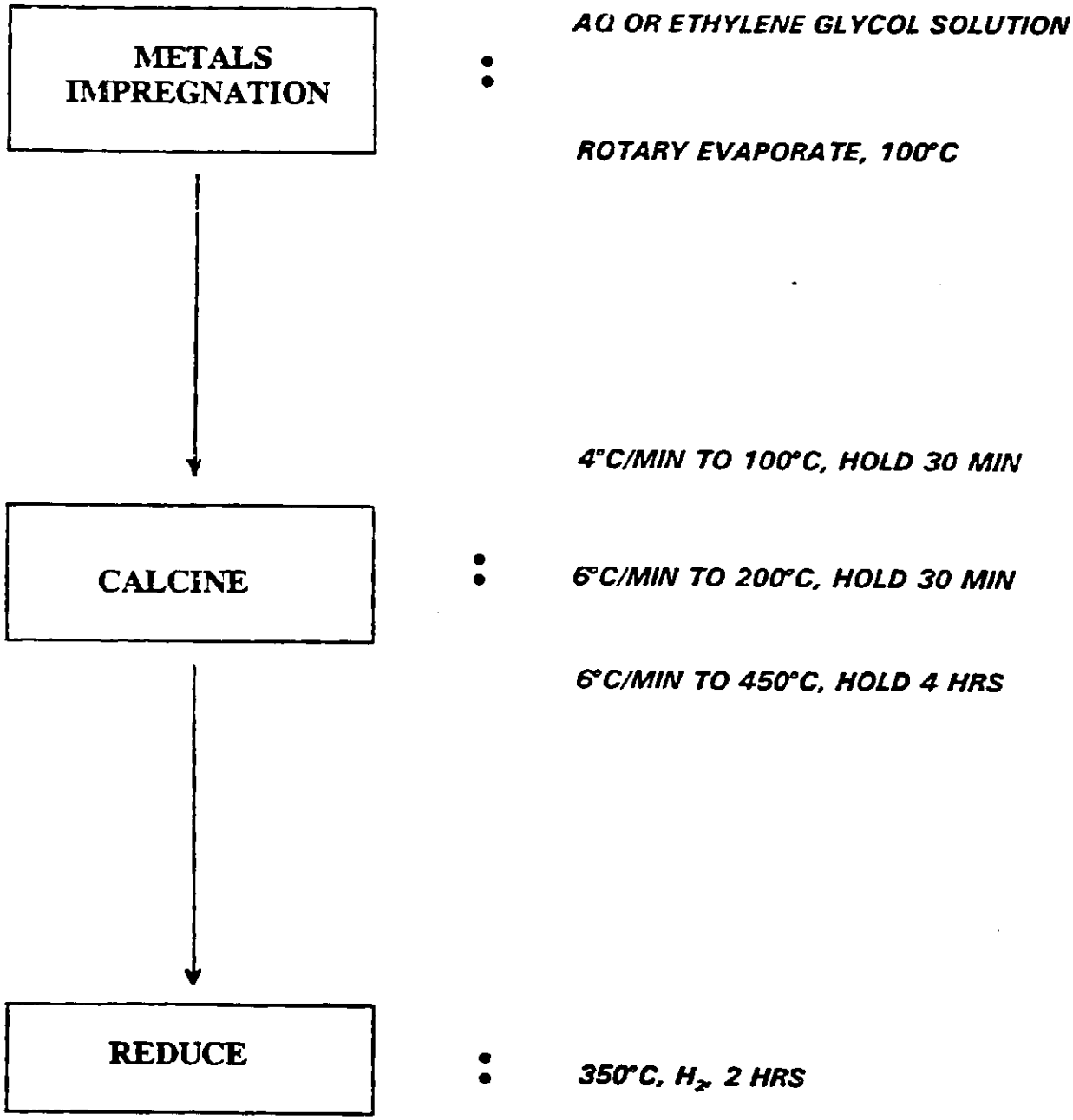


FIGURE A-2

PLT 700A RUN 95 Co,Mn,Zr,Re ON HCl Washed Y

6827-79 w/9.4% Co via eth-glycol pore fill

13g unreduced active in 160g quartz sand

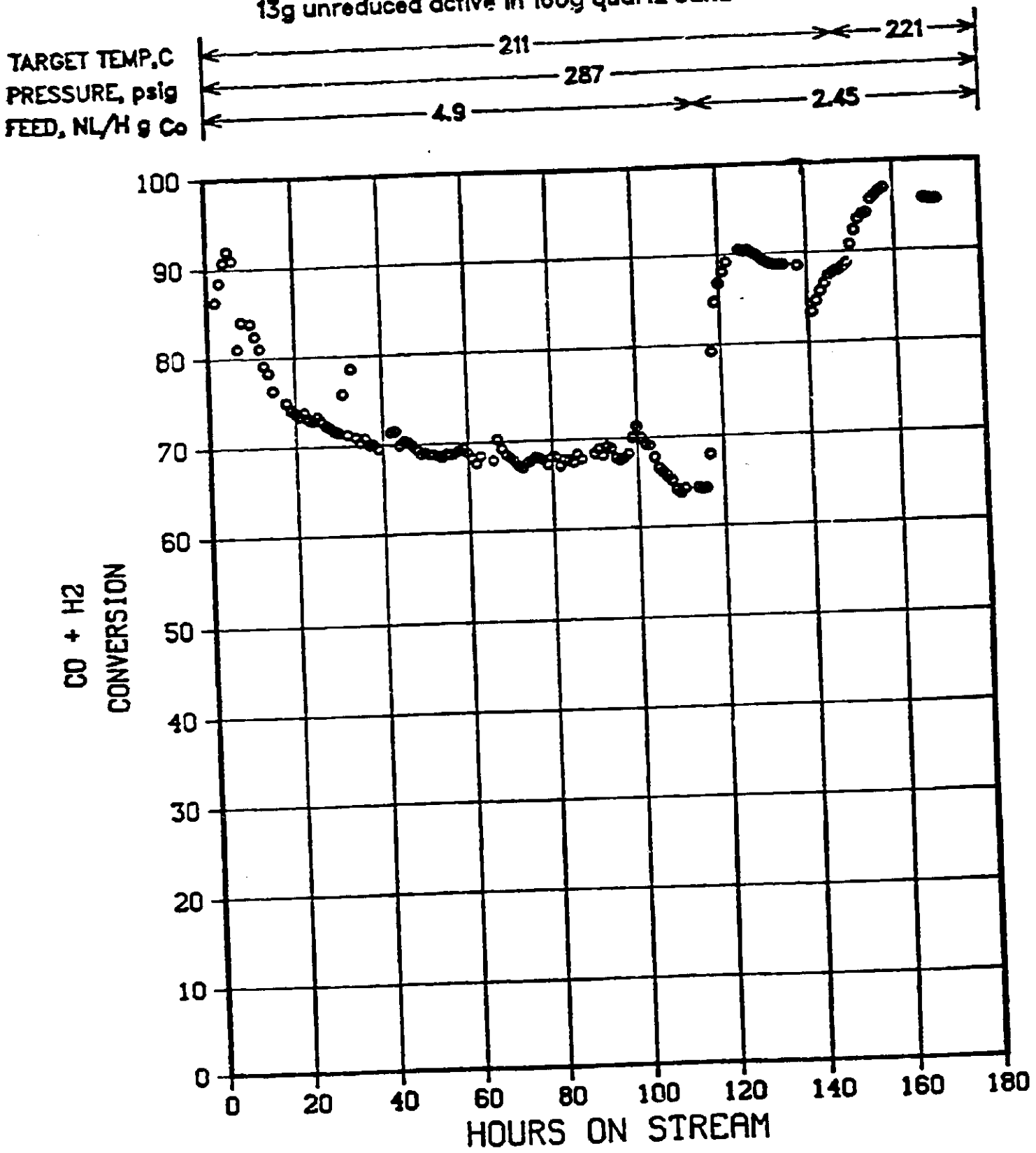


FIGURE A-3

PLI 700A RUN 95 Co,Mn,Zr,Re ON HCl Washed Y

6827-79 w/9.4% Co via eth-glycol pore fill

13g unreduced active in 160g quartz sand

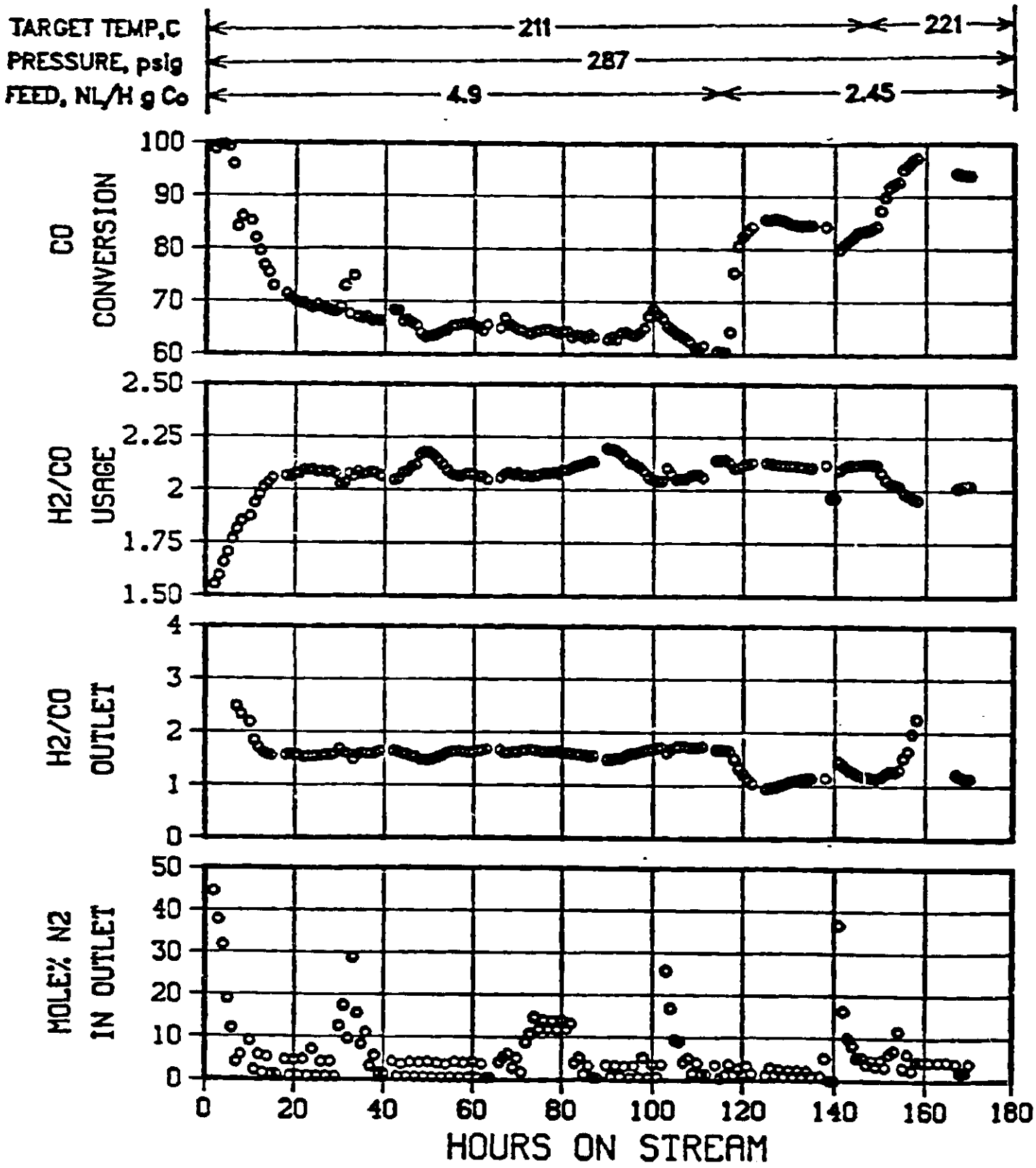


FIGURE A-4

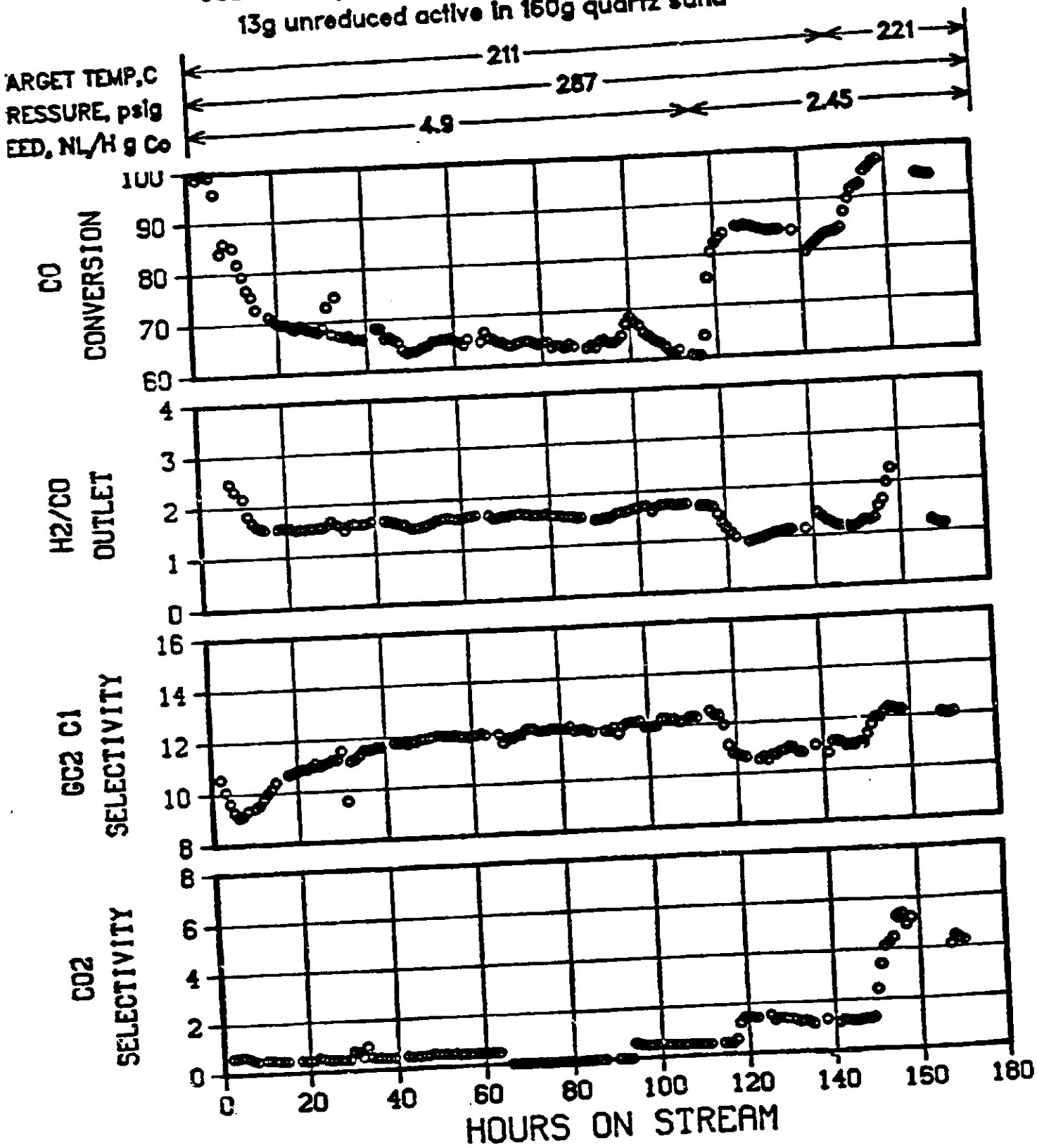

PLT 700A RUN 95 Co,Mn,Zr,Re ON HCl Washed Y
6827-79 w/9.4% Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand
221
211
287
245
4.9
ARGET TEMP,C
RESSURE, psig
EED, NL/H g Co
CO CONVERSION
H2/CO OUTLET
GC2 C1 SELECTIVITY
CO2 SELECTIVITY
HOURS ON STREAM

FIGURE A-5

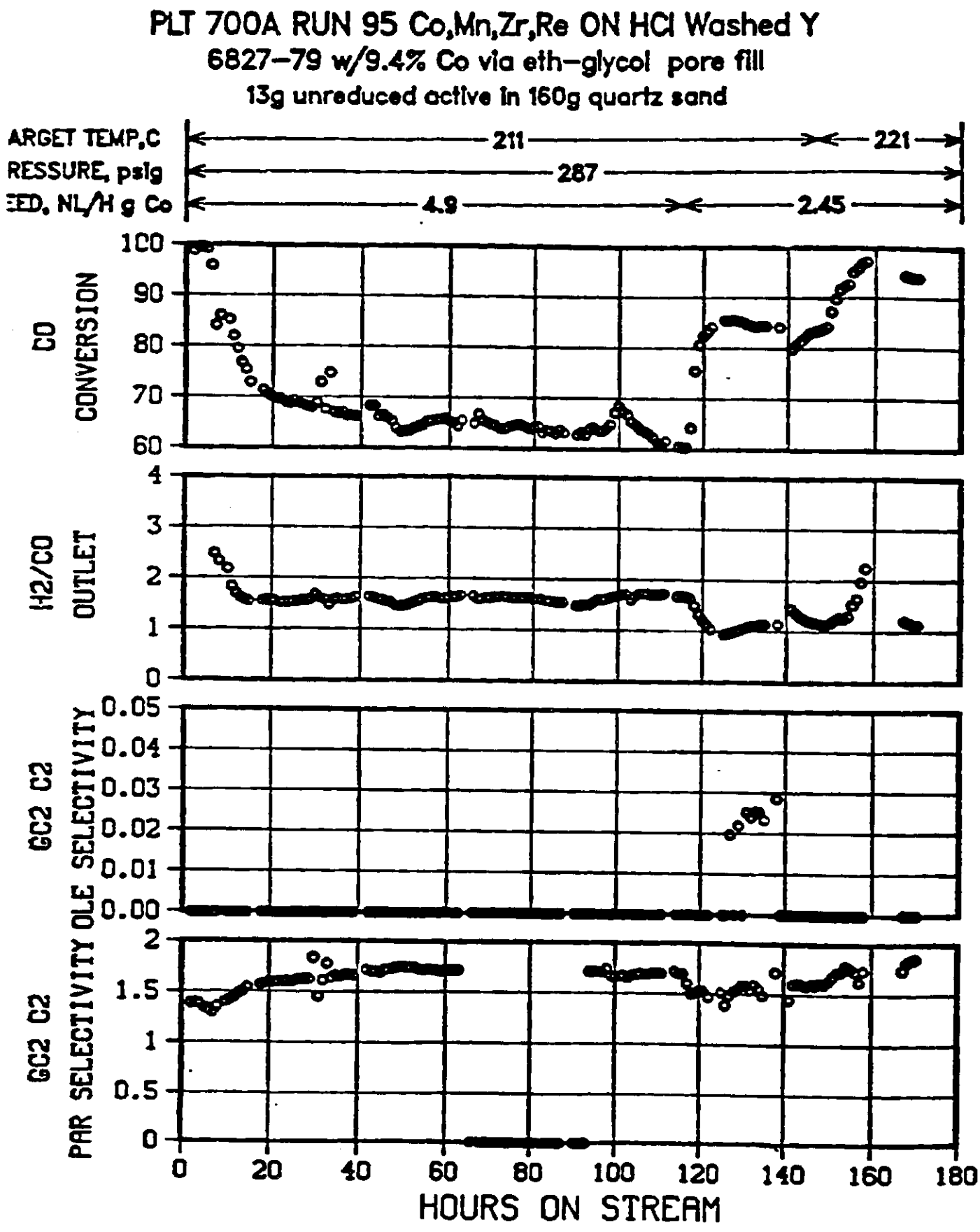

PLT 700A RUN 95 Co,Mn,Zr,Re ON HCl Washed Y
6827-79 w/9.4% Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand
ARGET TEMP,C
RESSURE, psig
ED, NL/H g Co
211
221
287
4.9
2.45
CO CONVERSION
H2/CO OUTLET
GC2 C2 PAR SELECTIVITY OLE SELECTIVITY
HOURS ON STREAM

FIGURE A-6

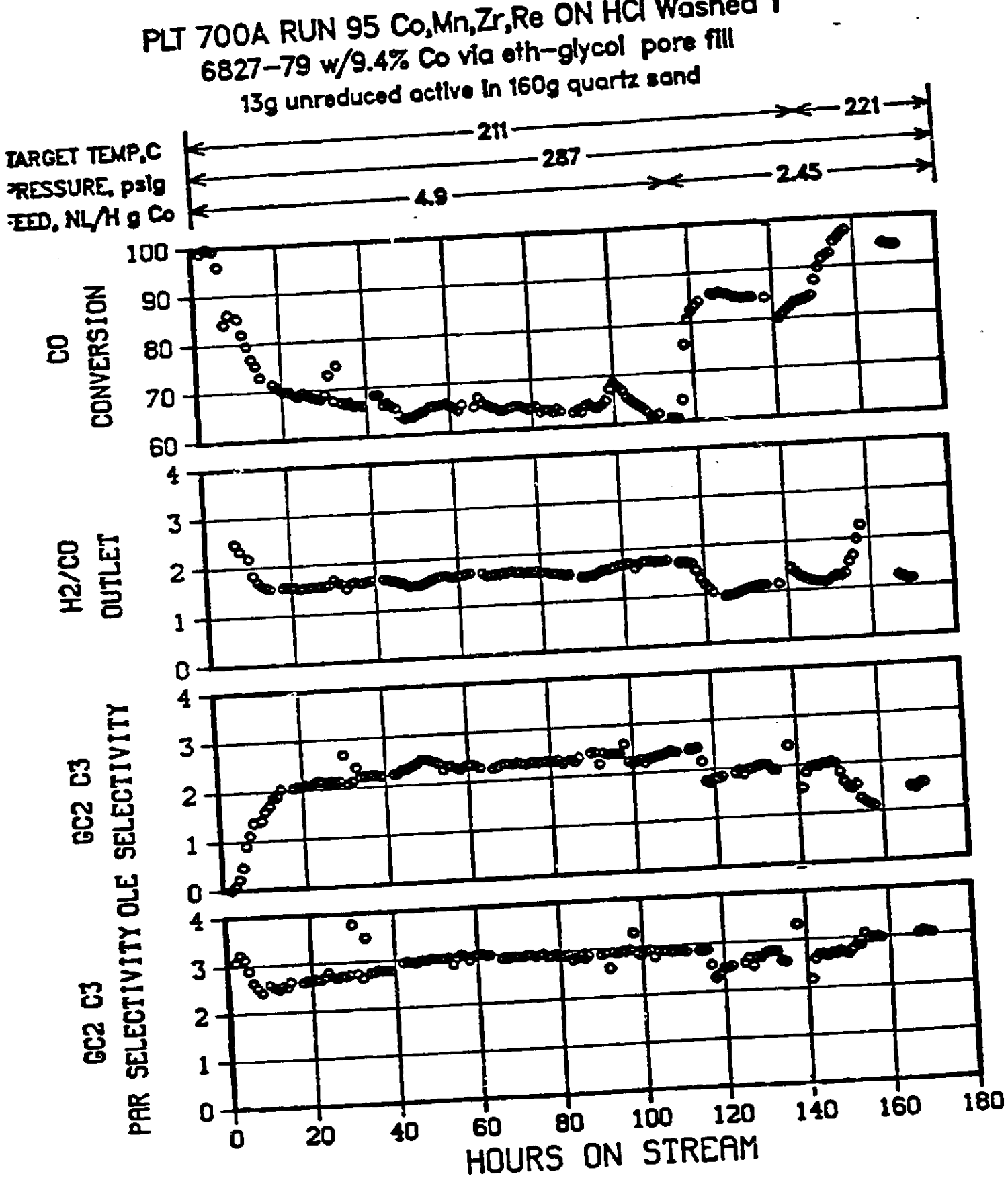

PLT 700A RUN 95 Co,Mn,Zr,Re ON HCl Washed Y
6827-79 w/9.4% Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand
TARGET TEMP,C
PRESSURE, psig
FEED, NL/H g Co
211
221
287
245
4.9
CO CONVERSION
H2/CO OUTLET
GC2 C3 PAR SELECTIVITY OLE
GC2 C3
HOURS ON STREAM

FIGURE A-7

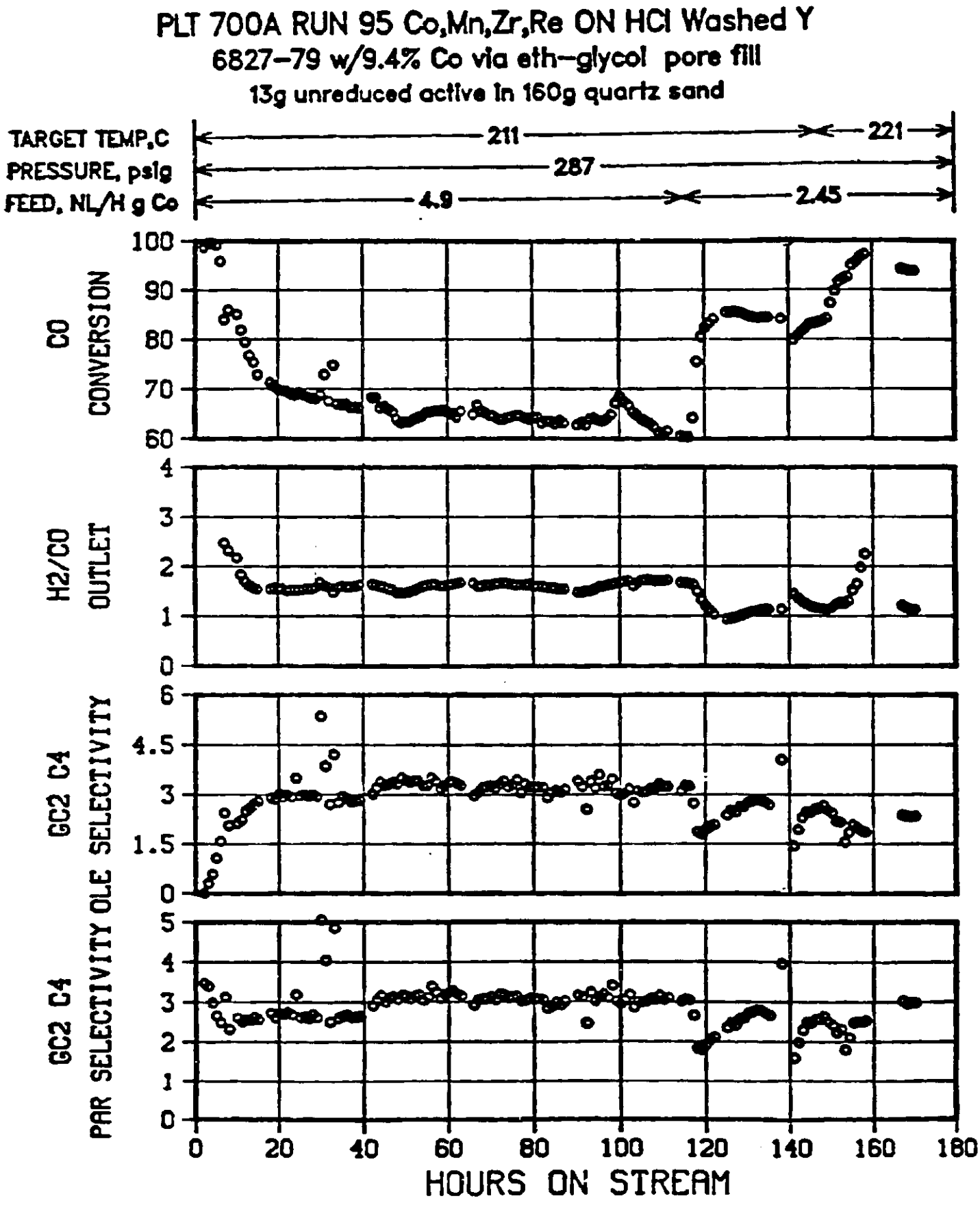

PLT 700A RUN 95 Co,Mn,Zr,Re ON HCl Washed Y
6827-79 w/9.4% Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand
TARGET TEMP,C
211
221
PRESSURE, psig
287
FEED, NL/H g Co
4.9
2.45
CO CONVERSION
100
90
80
70
60
H2/CO OUTLET
4
3
2
1
0
GC2 C4 PAR SELECTIVITY OLE SELECTIVITY
6
4.5
3
1.5
0
5
4
3
2
1
0
0
20
40
60
80
100
120
140
160
180
HOURS ON STREAM

FIGURE A-8

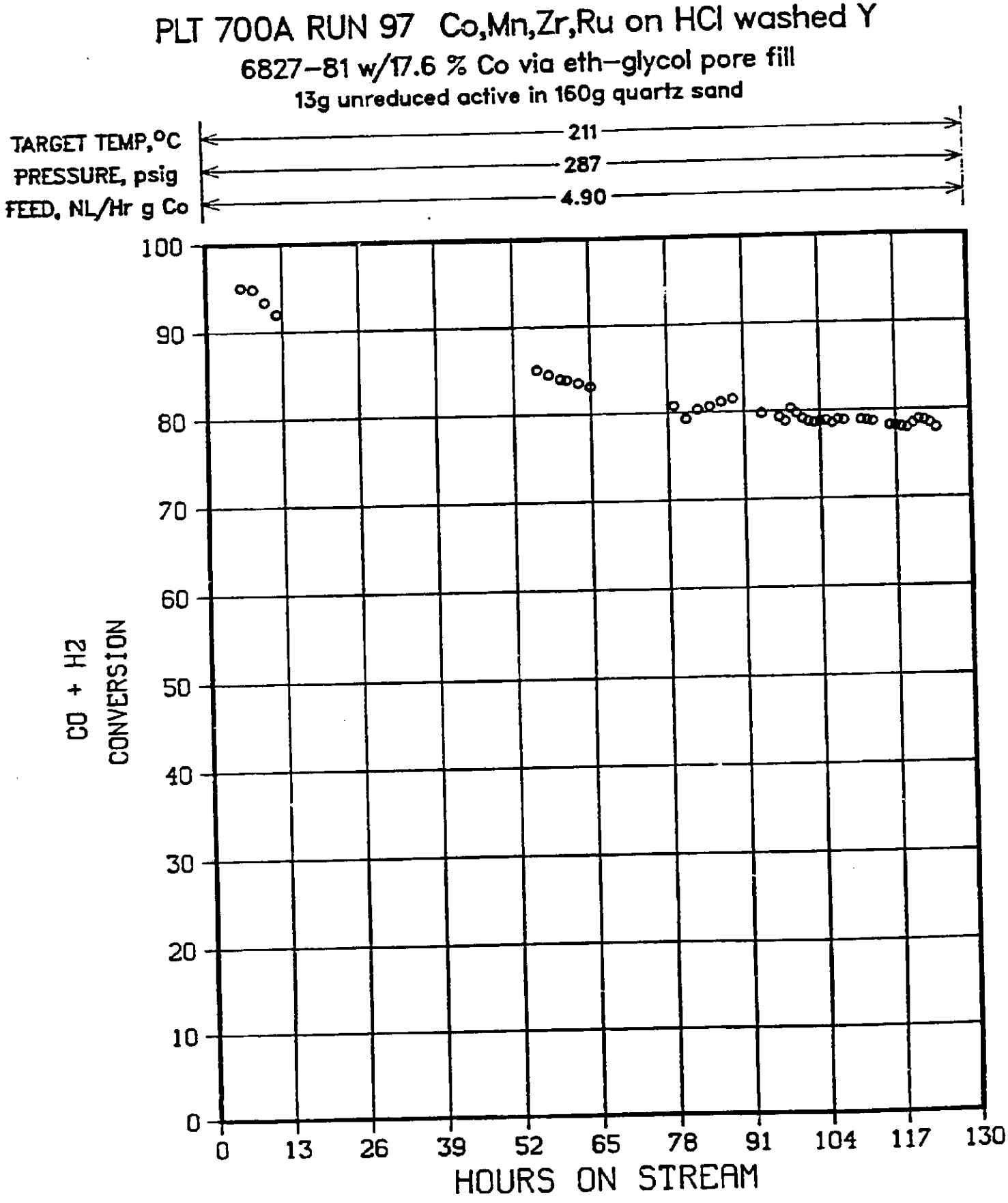

PLT 700A RUN 97 Co,Mn,Zr,Ru on HCl washed Y
6827-81 w/17.6 % Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand
TARGET TEMP,°C
PRESSURE, psig
FEED, NL/Hr g Co
211
287
4.90
CO + H2 CONVERSION
100
90
80
70
60
50
40
30
20
10
0
0
13
26
39
52
65
78
91
104
117
130
HOURS ON STREAM

FIGURE A-9

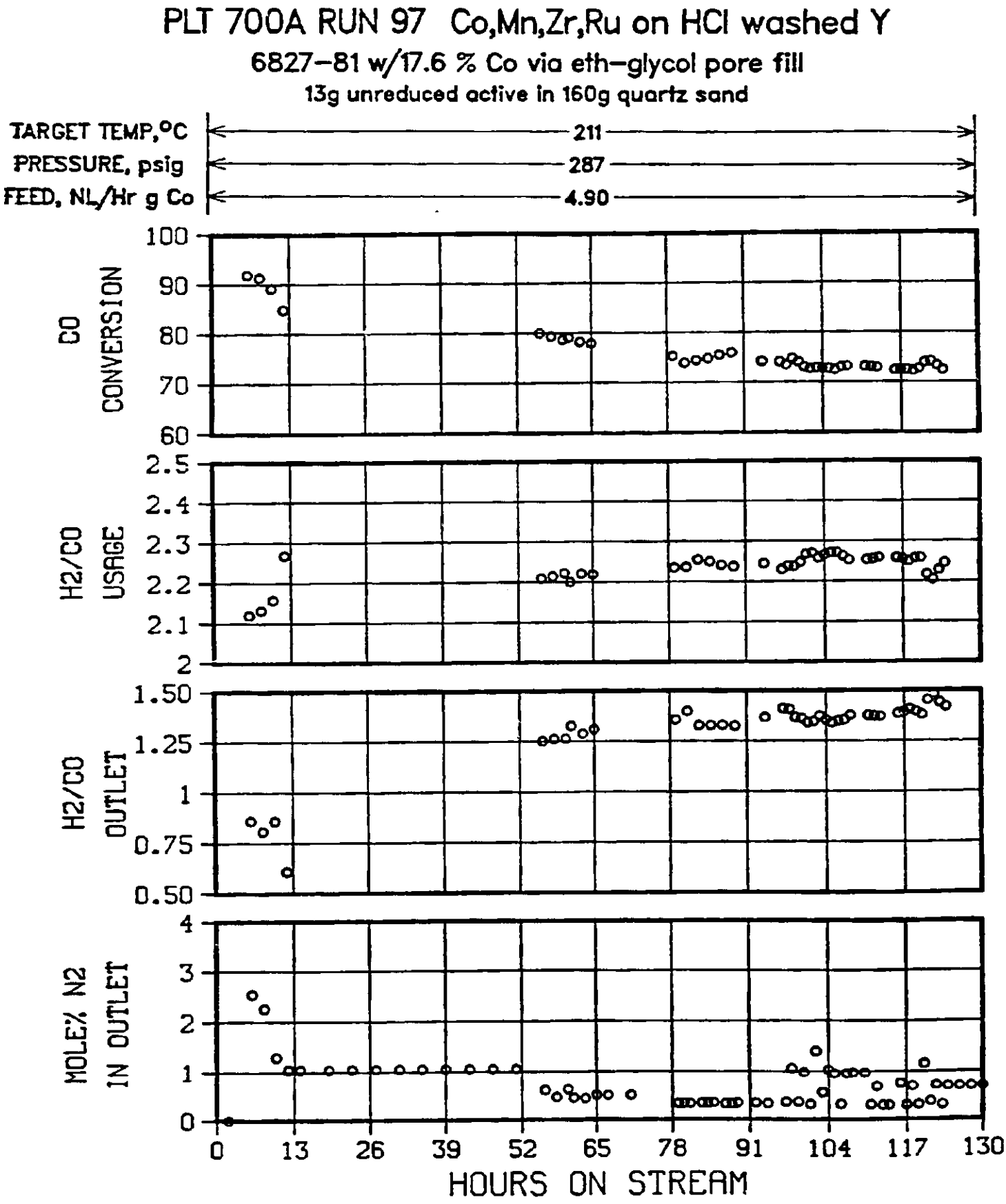

PLT 700A RUN 97 Co,Mn,Zr,Ru on HCl washed Y
6827-81 w/17.6 % Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand
TARGET TEMP,°C
PRESSURE, psig
FEED, NL/Hr g Co
211
287
4.90
CO CONVERSION
100
90
80
70
60
H2/CO USAGE
2.5
2.4
2.3
2.2
2.1
2
H2/CO OUTLET
1.50
1.25
1
0.75
0.50
MOLE% N2 IN OUTLET
4
3
2
1
0
0
13
26
39
52
65
78
91
104
117
130
HOURS ON STREAM

FIGURE A-10

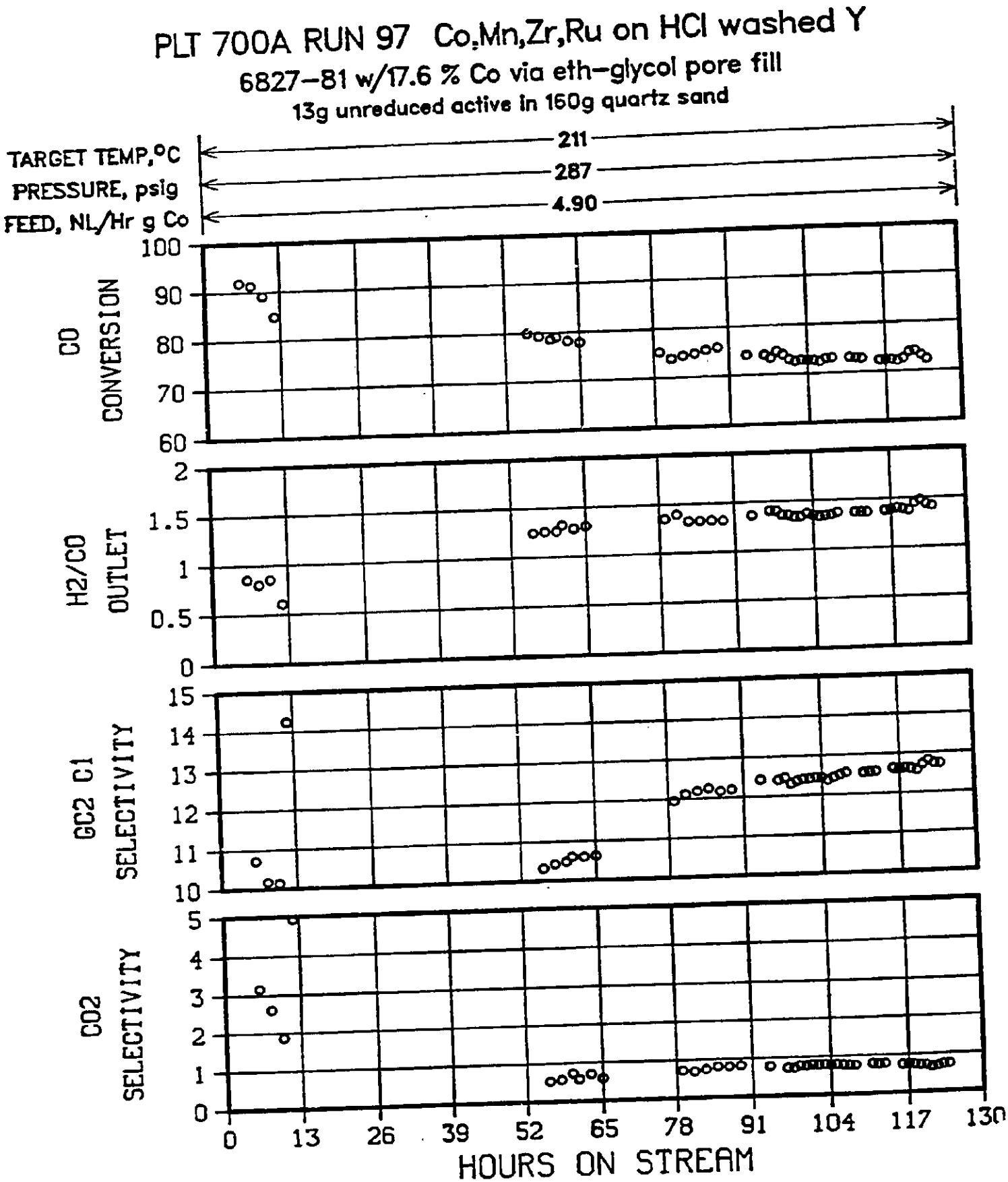

PLT 700A RUN 97 Co,Mn,Zr,Ru on HCl washed Y
6827-81 w/17.6 % Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand
TARGET TEMP,°C
PRESSURE, psig
FEED, NL/Hr g Co
211
287
4.90
CO CONVERSION
100
90
80
70
60
H2/CO OUTLET
2
1.5
1
0.5
0
GC2 C1 SELECTIVITY
15
14
13
12
11
10
CO2 SELECTIVITY
5
4
3
2
1
0
0
13
26
39
52
65
78
91
104
117
130
HOURS ON STREAM

FIGURE A-11

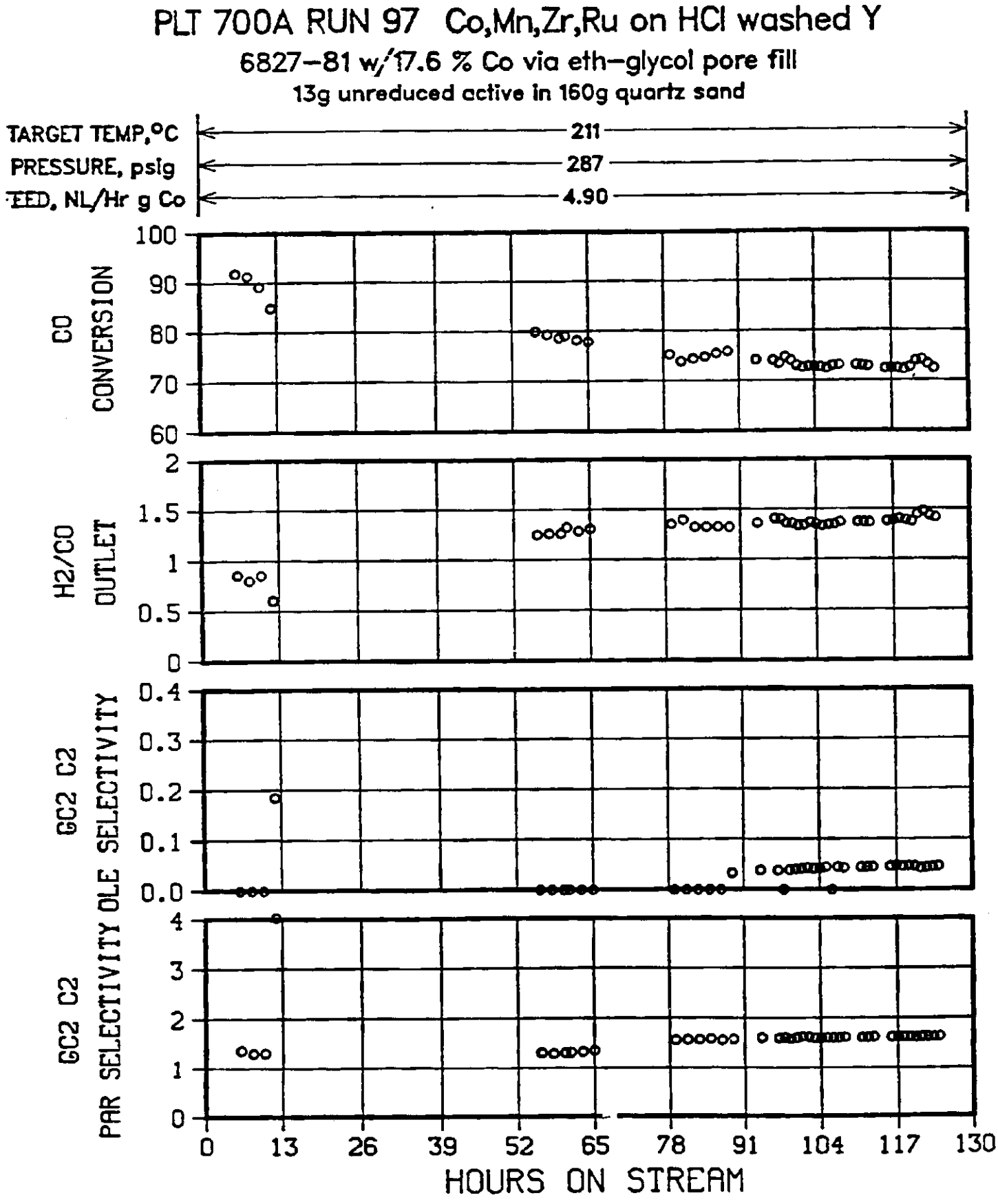

PLT 700A RUN 97 Co,Mn,Zr,Ru on HCl washed Y
6827-81 w/17.6 % Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand
TARGET TEMP,°C
PRESSURE, psig
FEED, NL/Hr g Co
211
287
4.90
CO CONVERSION
H2/CO OUTLET
GC2 C2 PAR SELECTIVITY OLE SELECTIVITY
HOURS ON STREAM

FIGURE A-12

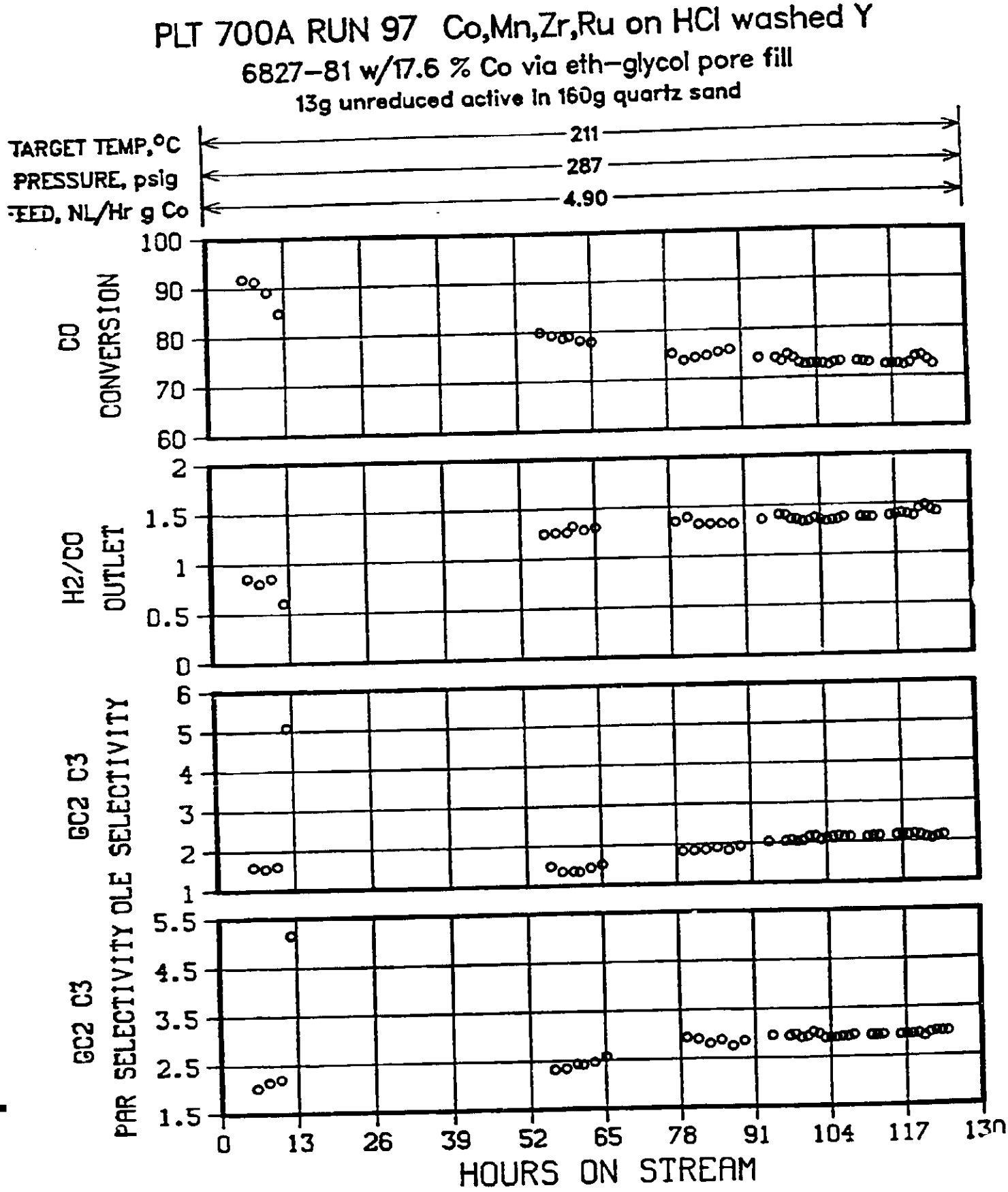

PLT 700A RUN 97 Co,Mn,Zr,Ru on HCl washed Y
6827-81 w/17.6 % Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand
TARGET TEMP,°C
PRESSURE, psig
FEED, NL/Hr g Co
211
287
4.90
CO CONVERSION
100
90
80
70
60
H2/CO OUTLET
2
1.5
1
0.5
0
PAR SELECTIVITY OLE SELECTIVITY
GC2 C3
6
5
4
3
2
1
GC2 C3
5.5
4.5
3.5
2.5
1.5
0
13
26
39
52
65
78
91
104
117
130
HOURS ON STREAM

FIGURE A-13

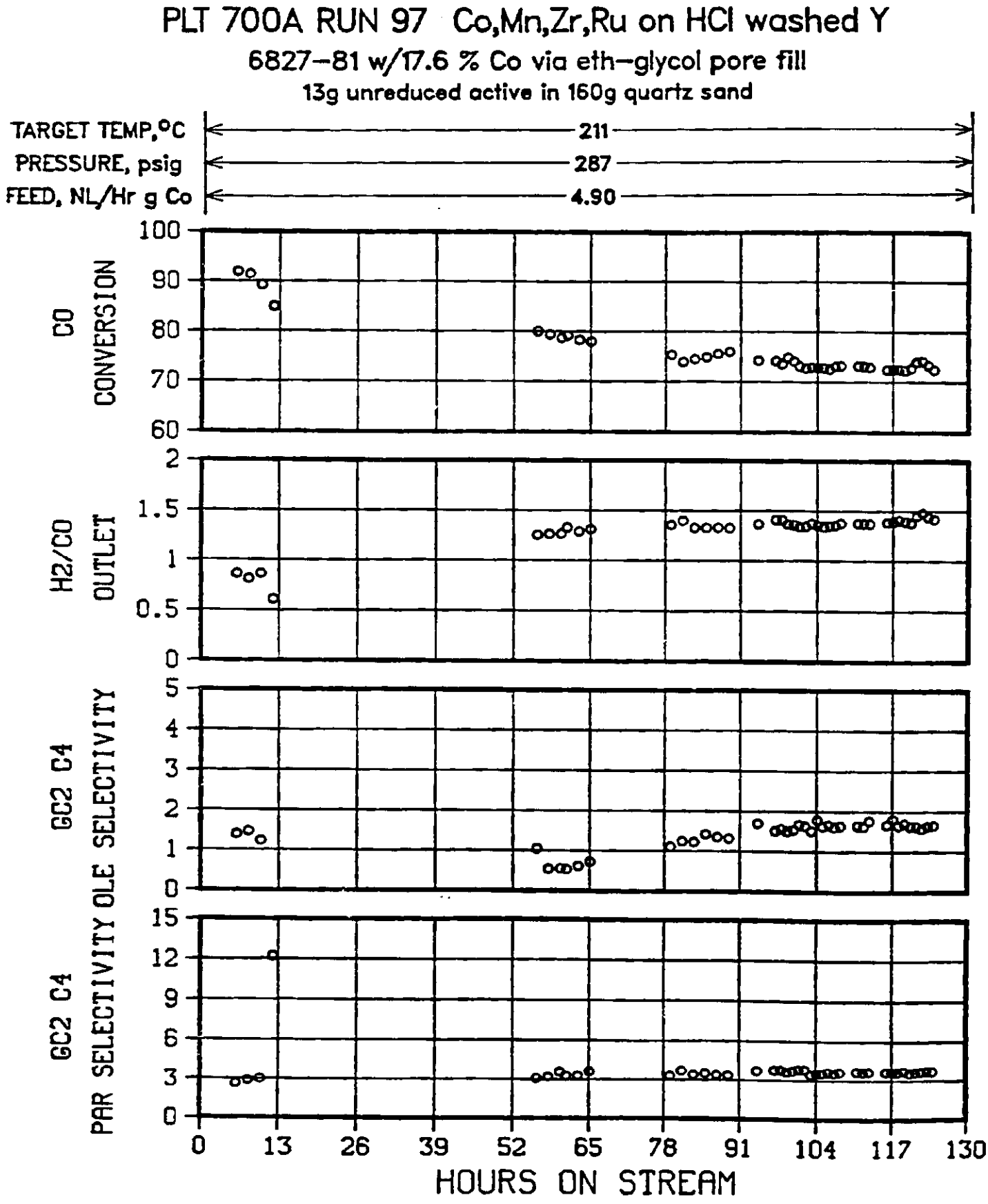

PLT 700A RUN 97 Co,Mn,Zr,Ru on HCl washed Y
6827-81 w/17.6 % Co via eth-glycol pore fill
13g unreduced active in 160g quartz sand
TARGET TEMP,°C
PRESSURE, psig
FEED, NL/Hr g Co
211
287
4.90
CO CONVERSION
H2/CO OUTLET
GC2 C4 PAR SELECTIVITY OLE SELECTIVITY
GC2 C4
HOURS ON STREAM

FIGURE A-14

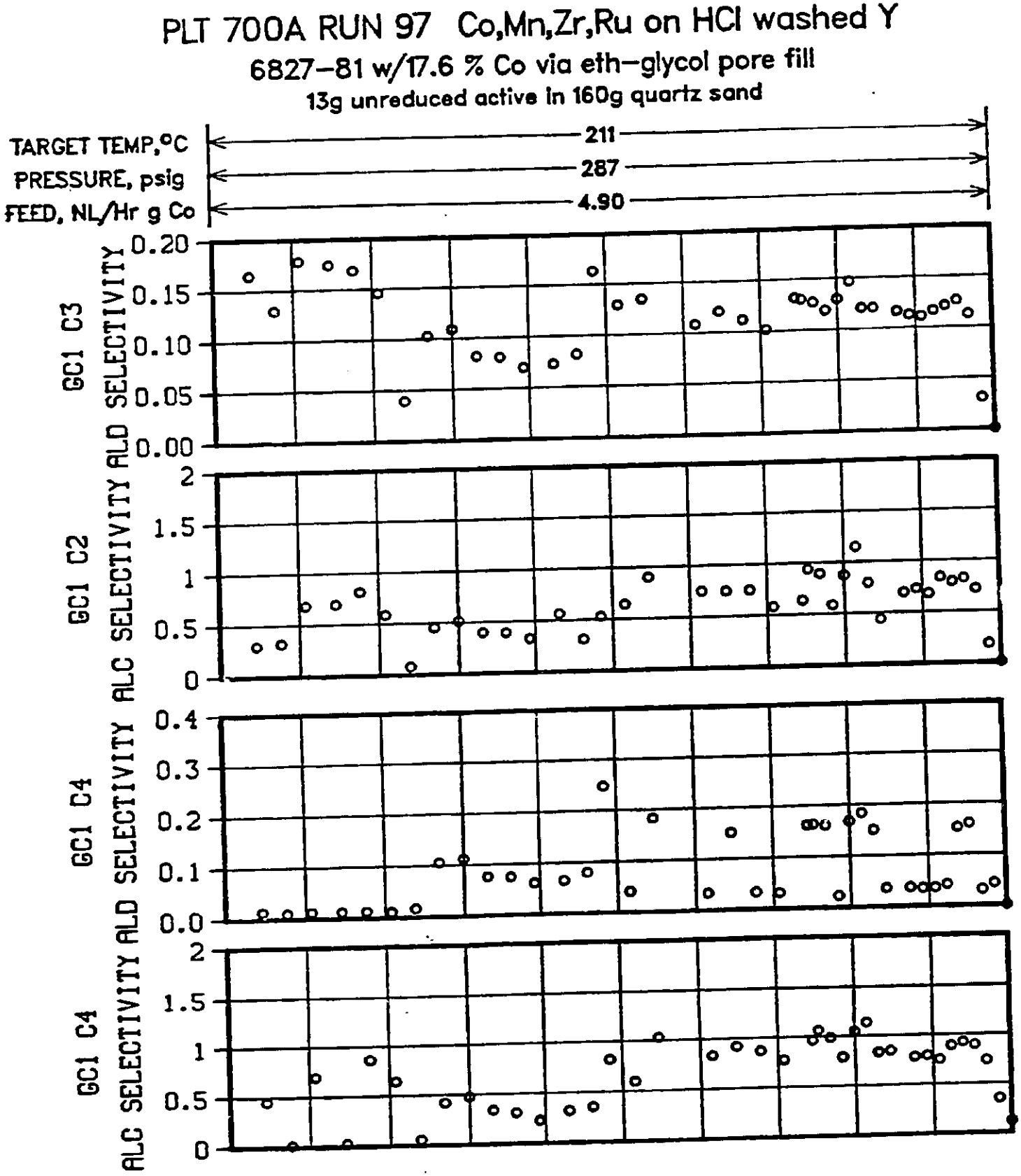
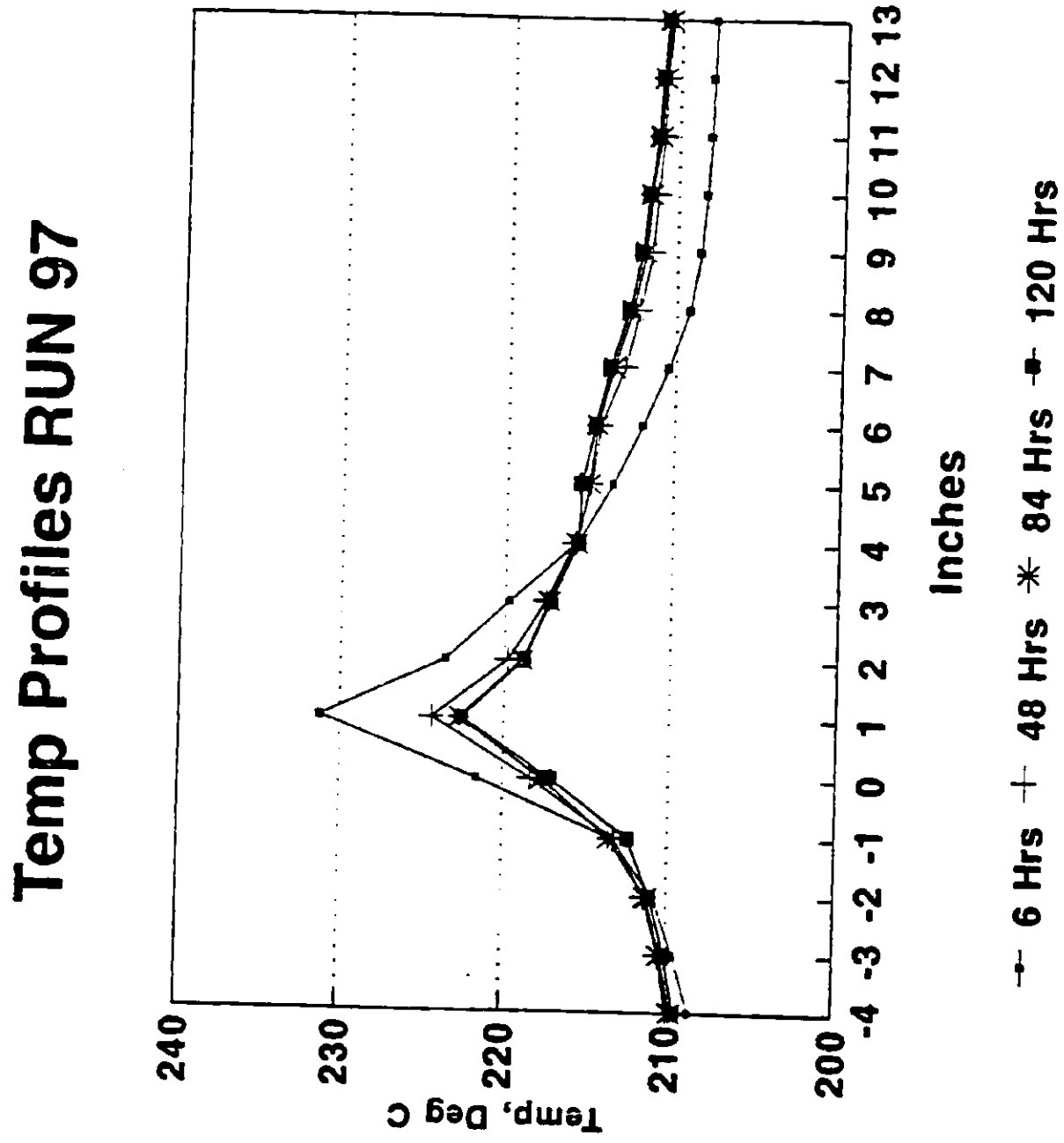

PLT 700A RUN 97 Co,Mn,Zr,Ru on HCl washed Y
6827–81 w/17.6 % Co via eth–glycol pore fill
13g unreduced active in 160g quartz sand
TARGET TEMP,°C
PRESSURE, psig
FEED, NL/Hr g Co
211
287
4.90
GC1 C3 ALD SELECTIVITY
0.20
0.15
0.10
0.05
0.00
GC1 C2 ALC SELECTIVITY
2
1.5
1
0.5
0
GC1 C4 ALD SELECTIVITY
0.4
0.3
0.2
0.1
0.0
GC1 C4 ALC SELECTIVITY
2
1.5
1
0.5
0

FIGURE A-15


Temp Profiles RUN 97
Temp, Deg C
240
230
220
210
200
-4 -3 -2 -1 0 1 2 3 4 5 6 7 8 9 10 11 12 13
Inches
6 Hrs
48 Hrs
84 Hrs
120 Hrs